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# Highly Photosensitive Daguerreotypes and their Reproduction: Physico-chemical Elucidation of Innovative Processes Developed Around 1840 in Vienna

Valentina Ljubić Tobisch*[a], Wolfgang Kautek *[a]

**Abstract:** *A physico-chemical elucidation of the world-wide first photographic technology allowing manifold reproduction is presented. An etched daguerreotype manufactured around 1840 in Vienna, preserved by the Technisches Museum Wien, served as a case-example. Surface analysis showed that the photographic process involved the formation of colloidal Ag nanoparticles (AgNPs) with sizes of 30-120nm with shell layers consisting of $Ag_2O$, $Ag_2S$, and some AgCl. The breakthrough photographic technique provided a hitherto unachieved high sensitivity due to various halogenide mixtures without Hg. The image development consisted in the reduction of the Ag halides by $H_2SO_3$ created by the hydrolysis of $S_2Cl_2$ leading to AgNPs adjacent to the latent image Ag nuclei. The fixation of the image was performed either by KCN or by $Na_2S_2O_3$. The investigated plate exhibits etched areas with $Ag_2O$ conversion layers and no Cl or S. The first reproduction method for daguerreotypes was invented by Joseph Berres in Vienna. It consisted in etching to enable printing. He applied a gum arabic solution on the fixed image surface. The gum arabic preferentially wetted the exposed AgNP regions so that unexposed areas could be etched by $HNO_3$.*

## Introduction

The French artist Louis Jacques Mandé Daguerre is considered the inventor of early photography[1–6]. His invention, publicly reported 1839 in Paris, marked the decisive step in the development of reproduction technology. During the preparation of the daguerreotype, a silver-plated surface was sensitized by silver iodine vapour and exposed to light in a camera. Then the plate was fumigated with mercury vapour and permanently fixed with a hot sodium thiosulfate solution[1,7–9]. At the beginning of the daguerreotype, long exposure times were a hindrance for the creation of the portraits and moving scenes like street views. On the one hand, this was due to the low light's optics available at the time, and on the other hand, to the relatively weak photosensitivity of the iodized silver surface. In order to reduce the exposure time and improve the photographic quality, further fundamental chemical and physical inventions had to be made[10].

Shortly afterwards, at the beginning of 1840is, remarkable inventions in the field of early photography have also been made in Vienna[11–17]. Josef Maximilian Petzval, a professor for mathematics, designed the very first photographic portrait objective lens (Fig. 1)[12–14,18,19]. This was the first mathematically calculated precision objective lens in the history of photography. Petzval's revolutionary dual lens exhibited a much higher luminous intensity and was more powerful than Daguerre's camera lens allowing exposure times of less than a minute. The lens was manufactured by the Viennese optician Peter Wilhelm Friedrich von Voigtländer. He developed a new camera equipped with Petzval's objective which was sold successfully worldwide.

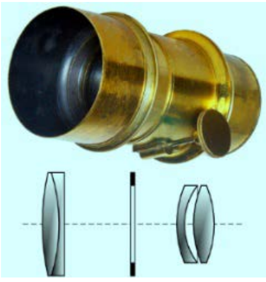

**Figure 1.** Petzval lens (objective). The first photographic portrait objective lens in the history of photography[18]. © Tamasflex.

Moreover, the Viennese photographic pioneers Franz Kratochwila and the medical doctors the brothers Johann and Josef Natterer developed new sensitization procedures in 1840/41 deviant from techniques applied in other countries[11–13,19] . In order to improve the poor light sensitivity of the iodized silver surface used by Daguerre, they developed sensitization procedures employing mixtures of bromine, chlorine and iodine applied in various sequences and compositions (Table 1). In this way snapshots could be taken for the first time[12]. The first two worldwide known photographs of street scenes and people crowds originate from them[3,13,14]. A representative fuming box and laboratory utensils for daguerreotype are depicted in Fig. 2a and Fig. 2b, respectively. In addition, the Natterer brothers developed another procedure omitting mercury used in common daguerreotype[12].

**Figure 2 left.** Fuming box for daguerreotype, Inv.Nr.: 2112, Technisches Museum Wien, Austria. **right.** Wooden box with laboratory utensils for daguerreotype, 1839 Giroux Paris, Inv.Nr.: 2110, © Technisches Museum Wien, Austria.

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**Table 1.** Daguerreotype processing steps reported in literature

| Processing steps | Chemical reactions | |
|---|---|---|
| Coating the Cu plate with Ag | | |
| Polishing | | |
| Sensitization with $I_2$ (L. Daguerre 1839)[1–3,10]<br>Multiple sensitization[1,11–13,16]:<br>$I_2 \rightarrow Br_2 \rightarrow I_2$<br>(J.F. Goddard 1840)<br>$I_2$=$Br_2$; $Cl_2$=$Br_2$; $I_2$=$Cl_2$; $I_2 \rightarrow Cl_2$<br>(F. Kratochwila, J. & J. Natterer, E. Waidele 1840/41)<br>$I_2 \rightarrow Br_2 \rightarrow Cl_2$<br>(F. Kratochwila, J. & J. Natterer 1840/41) | $2Ag_{(s)} + I_{2(g)} \rightarrow 2AgI$<br>$2Ag_{(s)} + Cl_{2(g)} \rightarrow 2AgCl$<br>$2Ag_{(s)} + Br_{2(g)} \rightarrow 2AgBr$ | Chemical acceleration of the Ag surface.<br>The surface is covered with Ag halogenide crystals. Halogenide mixture provides higher light sensitivity and shortens exposure time.<br>AgCl: white appearance<br>AgI: yellow appearance<br>AgBr: cream yellow appearance |
| Exposure of silver halides (AgX) | $10AgX + h\nu \rightarrow 2Ag_{5(s)} + 5\ X_{2(g)}$ | Decomposition of silver halides by light and formation of silver clusters (latent image formation) |
| Development by Hg vapour at ~ 60 – 120 °C<br>(L. Daguerre 1839)<br>Development without Hg (H. Becquerel 1840)[1] | $11Ag_5 + 45Hg_{(g)} \rightarrow 5Ag_{11}Hg_9$<br>$3Ag_5 + 20Hg_{(g)} \rightarrow 5Ag_3Hg_4$ | Silver react with hot mercury droplets and form stable amalgam.<br>Latent image developed by a yellow and/or red light treatment. |
| Fixation by sodium thiosulfate (J. Herschel 1839)[1–3,13,16] | $2\ Na_2S_2O_3 + AgX \rightarrow Na_3[Ag_8S_2O_3)_2] + NaX$ | Dissolution of unexposed residual silver halides. |
| Post cleaning with water | | Removal of the residual fixing solution |
| Gilding or toning with a AuCl solution[1–3,13,16] | $[Au(S_2O_3)_2]^{3-} + Ag \rightarrow Au + [Ag(S_2O_3)_2]^{3-}$ | Increasing contrast and brilliance of the image |
| Post cleaning with water | | Removal of the residual gold chloride solution |

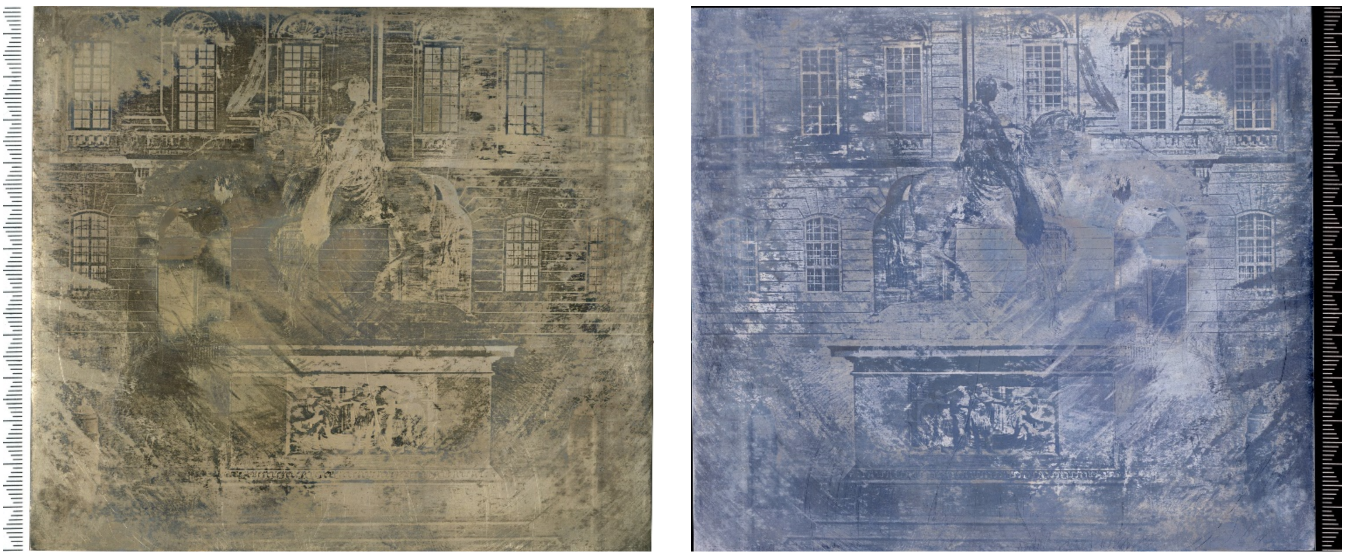

**Figure 3.** Joseph II's equestrian monument on Josefsplatz. Vienna. Etched Daguerreotype, Inv.Nr.: 83939/18, © Technisches Museum Wien, Austria. Plate size: 127 x 144 x 1 mm. **Left**: photograph. **Right**: inverted and horizontally mirrored photograph.

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The Austrian anatomy professor Joseph von Berres was interested in the generation of micrographs as a tool for microscopic research[13,17]. He recognized the potential of the newly discovered daguerreotype technique[20–23]. Since a daguerreotype is a unique object, Berres saw the need for the development of a reproduction technique. Already in 1840[3], he succeeded in producing printing plates for the first reproduction of photographs by etching daguerreotype plates. This etching technique is still widely unexplored, because no original etched daguerreotype plates have been discovered by now.

The knowledge of the physico-chemical processes associated with the above mentioned new photographic techniques is rudimentary up to date. The present study of the fundamentals of the above-mentioned novel procedures could be based on investigations of an etched daguerreotype plate probably photographed by the brothers Natterer and etched by Berres. It was recently discovered in the collection of the Technische Museum Wien [24]. This carrier plate is a silver-plated copper sheet typical for daguerreotypes and shows Joseph II's equestrian monument on Josefsplatz in Vienna (Fig. 3 left). Joseph II, the eldest son of the Austrian ruler Maria Theresa, was a Holy Roman Emperor and took over the Habsburg lands from his mother in 1780.

## Results and Discussion

### Surface Characterization

Surface characterization investigations were conducted in order to elucidate the manufacturing processes of daguerreotypes in Vienna of the early 1840s. The plate of the Joseph II's equestrian monument on Josefsplatz in Vienna retained its metallic brilliance (Fig. 3 left). The excellent depth of field and image quality despite the existing etched surface regions and various signs of aging can be best recognized by an inverted and horizontally mirrored photograph of the plate which represents the actual aspect on Josefsplatz. There, the camera was set up south of the monument at a window of Augustinertrakt, a side wing of the Hofburg, the former principal imperial palace (Fig. 3 right).

Optical micrographs and surface profilometry (Fig. 4) show that the daguerreotype plate represents an etched daguerreotype plate most probably designated for printing reproduction. Various profile levels - and even a flaw due to possibly an etchant splash - suggest this conclusion. The etched depressions are comparatively flat with a maximum depth of up to 6 µm.

A scanning secondary electron micrograph of the plate is shown in Fig. 5. In an EDX analysis, the primary electron beam interacts with the sample by repeated random scattering leading to a teardrop-shaped volume extending from less than 100 nm to approximately 5 µm into the near-surface region. The depth of this interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The depth of the x-ray (EDX) activation, $h$ can be appreciated by the following equation[25]

$$h = 0.0276\ m_a\ V^{1.67}\ /\ z^{0.89}\ \rho\ [\mu m] \tag{1}$$

where $m_a$ = atomic weight (g/mole), $\rho$ = density (g/cm$^3$), $z$ = atomic number, and $V$ = electron acceleration voltage (kV). With a $V$ of 20 kV and the respective values of Ag this relationship results in an EDX activation depth of ca. 1.4 µm. The silver coating on the copper substrate plate showed an average thickness of 7.3 ± 1.1 µm determined by an array of 36 x-ray fluorescence measurements spots. That shows that solely the Ag coating with an average thickness of 7.3 ± 1.1 µm has been analysed by EDX. A case

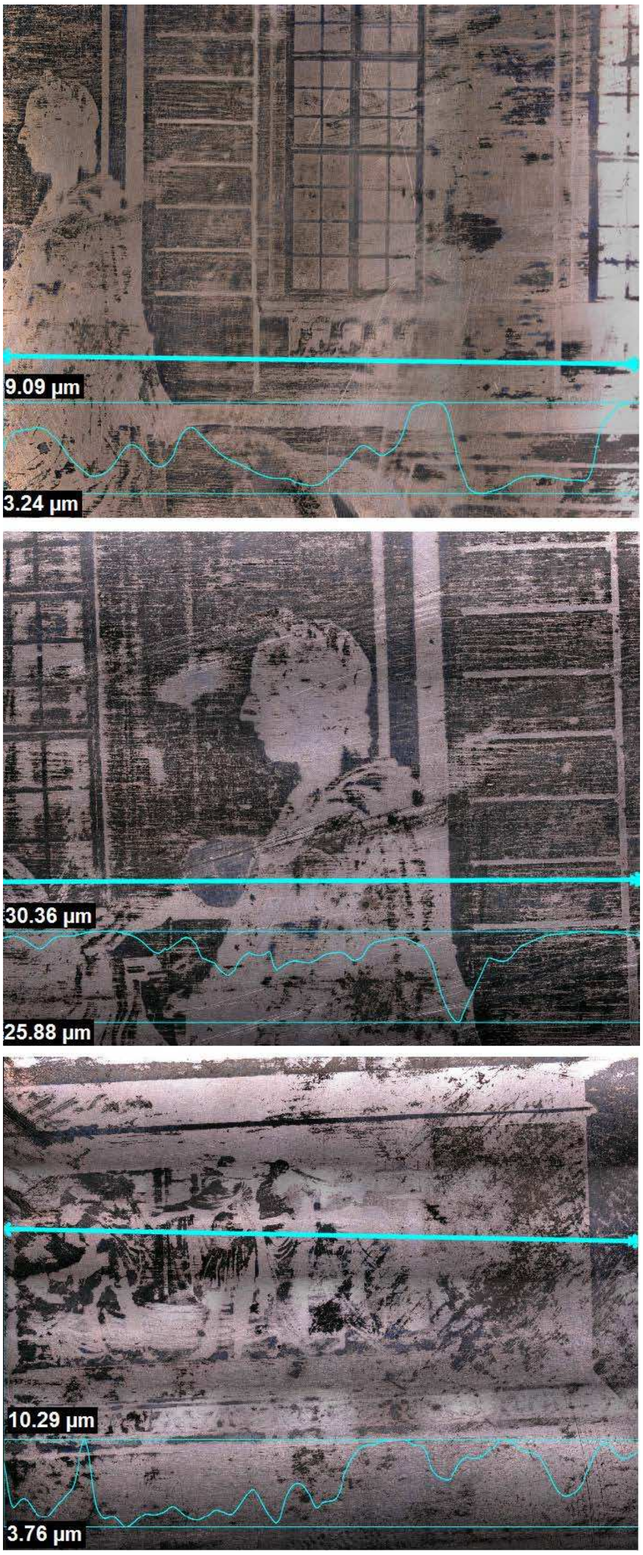


**Figure 4.** Optical micrographs with profilometry of the etched daguerreotype (Fig. 3). Three profile lines. Horizontal image edge: 513 mm (upper), 387 mm (middle), 272 mm (bottom).

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with finite Cu signals would suggest pores and/or inhomogeneities (e.g. due to etching) in the Ag layer.

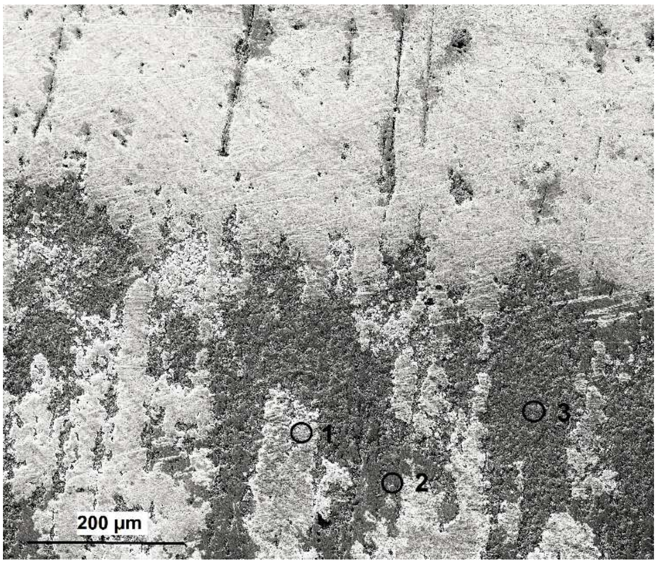


**Figure 5.** Scanning secondary electron micrograph of the etched daguerreotype (Fig. 3). Detail of the hoof front of the horse's right hindquarter. Three SEM/EDX measurement point are indicated.

Three SEM/EDX measurement points were chosen in the area of the hoof front of the horse's right hindquarter (Fig. 5). Three distinct morphological regions could be identified. Region 1 shows the highest secondary electron signal in contrast to region 2 and 3. This may suggest that the work function of this surface is lower than that of region 3, or/and that its lower conductivity leads to electron charging. A work function difference can be due to a different chemical composition of area 1 at variance to 2 and 3. The morphology of region 3 is typical for an etched surface which corresponds to low light exposure in contrast to the high exposure area 1 which does not exhibit etching features.

**Table 2.** EDX results (at%) of the regions 1-3 indicated in Fig. 5. Heliogravure on etched Daguerreotype.

| | Region 1 | Region 2 | Region 3 |
|---|---|---|---|
| S | 14.39 | 0 | 0 |
| Cl | 1.10 | 0 | 0 |
| Cu | 1.35 | 1.27 | 3.63 |
| O | 4.37 | 8.05 | 20.86 |
| Ag | 38.72 | 52.74 | 37.56 |
| C | 38.97 | 37.26 | 37.37 |
| Si | 0.57 | 0.68 | 0.57 |
| P | 0.53 | 0 | 0 |

Region 1 represents a well light-exposed area where the photographic process based on silver halogenides led to the photon-catalysed reduction to colloidal silver nanoparticles (AgNPs). This photoproduct can be clearly seen in Fig. 6 left. The observed particle size distribution is between 30 nm and 120 nm, which is less than in characteristic daguerreotype highlight image microstructures between 100 nm and 2.5 µm[1,5]. Particularly the top AgNPs appear light and blurred indicating electronic charging possibly due to core-shell NP morphologies with insulating shell compositions. Such chemical conversions of the Ag core can be recognized by the EDX analysis resulting in a significant sulphur and a moderate chlorine signal besides oxygen (Fig. 6 right, Table 2). This finding suggests that the colloidal particles exhibited a conversion shell layer consisting of $Ag_2O$, $Ag_2S$, and some AgCl with low conductivity.

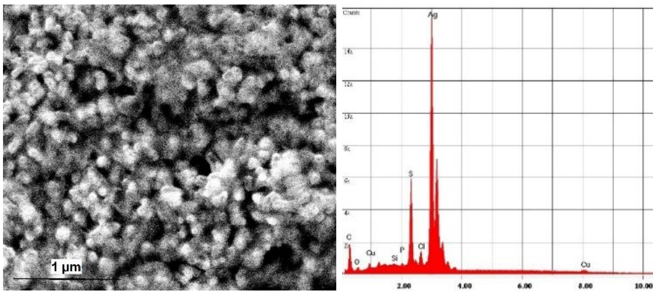


**Figure 6.** Scanning secondary electron micrograph (left) and EDX spectrum (right) of the etched daguerreotype (Fig. 3). Measurement point 1 in the white highlight.

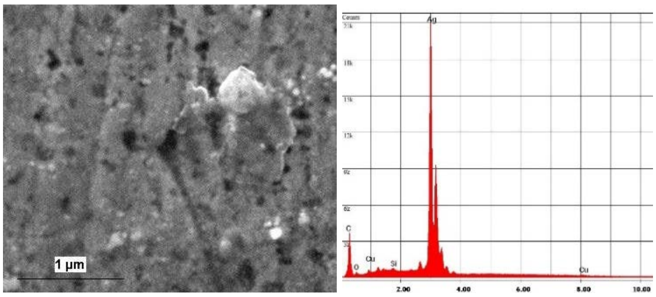


**Figure 7.** Scanning secondary electron micrograph (left) and EDX spectrum (right) of the etched daguerreotype (Fig. 3). Measurement point 2 in the midtone area.

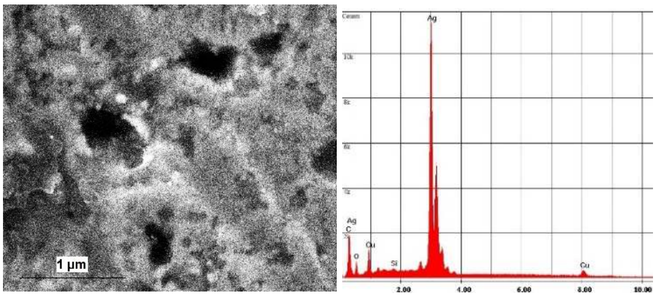


**Figure 8.** Scanning secondary electron micrograph (left) and EDX spectrum (right) of the etched daguerreotype (Fig. 3). Measurement point 3 in the shadow area.

These AgNPs and their conversion shells are practically absent in the midtone (Region 2) and dark tone (Region 3) areas (Fig. 5). The midtone region shows only some scratches from the original polishing treatment and some etching bits with diameters of < 100 nm (Fig. 7 left). The dark tone areas, in contrast, are dominated by larger etching bits with diameters of 200 – 400 nm (Fig. 8 left).

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Original polishing scratches are still observable despite extensive etching, however widened. The EDX analysis showed that any conversion layers involving Cl or S are absent (Fig. 7 right, 8 right, Table 2). The increased oxygen signal of the most extensively etched surface (Region 3, Fig. 8 right, Table 2) indicates a more abundant $Ag_2O$ layer. The etching process exposed some copper substrate which is indicated by a somewhat higher Cu signal.

## Photographic Procedure reconstruction

### *Silver Coating of the Copper Plate*

Solid silver plates were rarely used [12]. In the beginning 1840ies galvanic silver plating was employed[1] and were available at relatively high costs in Vienna. Therefore, Kratochvila, J. and J. Natterer chose also electroless plating[26,27]. AgCl was dissolved in a NaCl solution[28]. Solid AgCl can form a chloroanion in the presence of highly concentrated $Cl^-$ [29,30]

$$AgCl + Cl^- \rightarrow [AgCl_2]^- \quad (2)$$

The electroless reaction was the cementation of Ag from the dichloro silver anion on the copper plate. This is thermodynamically driven by the oxidative power of the silver electrode[31]:

$$Ag \rightleftharpoons Ag^+ + e^- \quad (U_0 = +0.80\ V) \quad (3)$$

with a standard potential $U_0$ which is much more positive than that of the Cu dissolution reactions

$$Cu \rightleftharpoons Cu_2^+ + 2\ e^- \quad (U_0 = +0.34\ V) \quad (4)$$

$$Cu \rightleftharpoons Cu^+ + e^- \quad (U_0 = +0.52\ V) \quad (5)$$

The overall electroless silver plating reaction (a cementation reaction) is therefore

$$[AgCl_2]^- + Cu \rightarrow Cu^+ + 2\ Cl^- + Ag \quad (6)$$

or

$$2\ [AgCl_2]^- + Cu \rightarrow Cu_2^+ + 4\ Cl^- + 2\ Ag \quad (7)$$

### *Sensitization*

The first sensitization process based on the Daguerre's experience was the fumigation of the polished silver surface with iodine vapour[1–3,13] in a special fuming box (Fig. 2 left). There, photosensitive AgI was generated by the oxidation of the Ag substrate[5] (Table 1). However, iodine does not exhibit a sufficiently positive electrochemical potential for this reaction. An indirect route via the oxidant iodate can be suggested. It is well established that aqueous iodine chemistry is mainly governed by three reactions[10,32], namely the disproportionation of iodine to hypoiodous acid HIO, or hypoiodide $IO^-$ anions (oxidation state +I), and to iodide,

$$I_2 + H_2O \rightarrow I^- + IO^- + 2\ H^+. \quad (8)$$

Hypoiodide is not stable and disproportionates to iodate (oxidation state +V) and iodide,

$$3\ IO^- \rightarrow 2\ I^- + IO_3^- \quad (9)$$

The overall reaction is

$$3\ I_2 + 3\ H_2O \rightarrow 2\ I^- + IO_3^- + 6\ H^+ \quad (10)$$

The oxidative power of the $IO_3^-$ ion is sufficient at all applied pHs (mostly near neutrality)[33,34] to oxidize the Ag surface so that AgI can be formed as a photosensitive film:

$$6\ Ag + IO_3^- + 6\ H^+ \rightarrow 6\ AgI + 3\ H_2O \quad (11)$$

AgI exhibited a very low sensitivity[1,3].

A multiple sensitization by fumigation with bromine in addition to iodine was introduced practically in parallel by laboratories in England and Austria yielding an improved sensitivity[2,3,11,13]. Bromine, in contrast to iodine shows a sufficiently positive standard potential[31]:

$$Br_2 + 2\ e^- \rightleftharpoons 2\ Br^- \quad (U_0 = +1.0873\ V) \quad (12)$$

so that Ag ($U_0$ = +0.80 V) can be oxidized directly to the photosensitive phase AgBr.

The Viennese pioneers, F. Kratochwila, the brothers Natterer, and E. Waidele, extended the multiple sensitization procedures of photographic plates with chlorine gas[11–13,15]. They employed $Cl_2$ and $Br_2$ or $I_2$ concurrently, or in a series, first $I_2$ followed by $Cl_2$, or first $I_2$ followed by $Br_2$ and finally $Cl_2$.

The iodized surface was exposed to $Cl_2$ gas produced by a chlorinated lime ("Chlorkalk"), a mixture of calcium hypochlorite, $Ca(OCl)_2$, $CaCl_2$ and a $Ca(OH)_2$ solution[11]. The reactant of this mixture is CaCl(OCl). It can react with an acid such as carbonic acid from the atmospheric $CO_2$ producing $Cl_2$:

$$CaCl(OCl) + CO_2 \rightarrow CaCO_3 + Cl_2. \quad (13)$$

$Cl_2$ easily can oxidize the Ag surface due to its very positive potential

$$Cl_2 + 2\ e^- \rightleftharpoons 2\ Cl^- \quad (U_0 = +1.36\ V) \quad (14)$$

resulting in an AgCl film.

### *Exposure*

The Viennese authors thus employed a silver halogenide (AgX) mixture as photosensitive phase[11]. The absorption of a photon results in the formation of a latent image based on Ag4 clusters[35]. A photoreaction can be assumed as follows:

$$8\ AgX + 4\ h\nu \rightarrow 2\ Ag_4 + 4\ X_2 \quad (15)$$

The exposure time in a Voigtländer's Camera Obscura was only within 5 s to 6 s in cloudy weather, within 2 s on a bright day, and in direct sunlight in an "unmeasurable" time. This novel technology allowed the unblurred high quality imaging of moving motifs such as portraits and street scenes for the first time.

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***Development***

The common development procedure for daguerreotypes was the formation of Ag amalgam particles next to the latent image Ag clusters[1,36]. The heated Ag plate was treated by Hg vapour.

Edmont Becquerel reported a development procedure based on AgI without the use of mercury in 1840. This method is related to the famous “Becquerel effect”[37] where AgI was exposed resulting in a latent image. This was further developed by a yellow and/or red light treatment. However, this ground-breaking invention did not yet assert itself against the method of Daguerre employing mercury[1,3,13].

In the following year, in 1841, also the Viennese Natterer brothers developed a method without mercury[12]. This novel procedure represented a breakthrough photographic technique due to the high sensitivity of the employed halogenide mixture. In the case of the least sensitive layer of AgI, a development procedure was reported[15]. This development process can be reconstructed as follows (comp.[38,39]):

$$2\ S_2Cl_2 + 2\ H_2O \rightarrow SO_2 + 4\ HCl + 3/8\ S_8. \qquad (16)$$

The resulting $SO_2$ vapour reacts at the surface in humid atmosphere to sulphurous acid:

$$SO_2 + H_2O \rightarrow H_2SO_3. \qquad (17)$$

It is remarkable that the deposition of the developer substance, sulphurous acid, was applied before the exposure. The sulphurous acid obviously acted as a reductant for the Ag halide (AgX) leading to AgNPs around the latent image Ag nuclei:

$$2\ AgX + H_2SO_3 + H_2O \rightarrow 2\ Ag + 2\ HX + H_2SO_4 \qquad (18)$$

The development process already took place in the camera [28].

The authors even used sulphur bromide instead of sulphur chloride,

$$2\ S_2Br_2 + 2\ H_2O \rightarrow SO_2 + 4\ HBr + 3/8\ S_8, \qquad (19)$$

and claimed a superb sensitivity[19].

***Fixation***

Josef Natterer performed the fixation either by potassium cyanide, KCN, or by sodium thiosulphate[19], $Na_2S_2O_3$. The fixation consisted in the dissolution of remnant halides:

$$2\ Na_2S_2O_3 + AgX \rightarrow Na_3[Ag(S_2O_3)_2] + NaX \qquad (20)$$

$$4\ KCN + 2\ AgX \rightarrow 2\ K[Ag(CN)_2] + 2\ KX \qquad (21)$$

***Etching***

The Viennese Joseph Berres succeeded in developing an etching technique in 1840 enabling first reproductions of the newly invented photographs[20–22,40]. He observed that the exposed Hg/Ag areas showed a high resistance towards etching with nitric acid. The unexposed areas covered by unreacted AgX could be attacked by the acid. His treatment of the exposed plates consisted of two operations, (1) the permanent fixation of the image and (2) the etching. The special image fixation procedure is passed down as follows[21].

Berres’s fixation deviated from Natterer’s procedure in that it prepared the follow-up etching step. The treatment of the plates in $HNO_3$ led to some dissolution of Cu at the reverse side and Ag on the exposed front side:

$$3\ Cu + 2\ NO_3^- + 8\ H^+ \rightarrow 3\ Cu_2^+ + 4\ H_2O + 2\ NO \qquad (22)$$

$$3\ Ag + NO_3^- + 6\ H^+ \rightarrow 3\ Ag^+ + 3\ H_2O + NO \qquad (23)$$

Due to its corrosive and oxidative effect, nitric acid is often used in printing technology for etching and is the oldest known mordant.

After fixing the image, Berres continues with the etching process[21].

In this second operation step (the “etching” step), a gum arabic solution was applied on the fixed image surface. Gum arabic, a mixture of glycoproteins and polysaccharides mainly consisting of arabinose and galactose, showed different wetting on the exposed AgNP regions and the unexposed bulk Ag regions. Obviously, the wetting was drastically reduced on the unexposed polycrystalline Ag region so that the follow-up etching step preferentially attacked the substrate. The formed depressions could accept the printing ink in the follow-up reproduction step. On the other hand, the exposed AgNP regions were much more wetted and thus protected by a stable gum arabic film.

In his report on the new developements in daguerreotype[19], Berres pointed to an important detail in the preparation of daguerreotype plates destined for later etching. Although it has been claimed that any carefully applied cleaning method or any cleaning agent could achieve a pure plate and a satisfactory image, he points out that the challenge of the daguerreotype process lies in the cleaning of the plates. Two techniques by Kratochwila and the physicist Anton Martin (1812-1882) were rated by him as the most reliable ones. Kratochwila simplified and shortened the time-consuming cleaning process by cleaning the polished plate with a distilled turpentine oil and cotton, followed by polishing with a bale of deerskin. Martin cleaned the plates with ethyl alcohol, distilled water, and powdered sheep bones on a soft deerskin. According to Berres, Martin's images exhibit an unsurpassed clarity and sharpness, and are recommended for the production of heliographies destined for printing. The turpentine-treated plates often still had a mist that made the image less pure and, due to a fine resin coating, prevented deeper penetration of the etching process[19].

Berres improved his etching procedure[19]. Obviously, Berres experimented also with amalgamated images[19]. The etch process was repeated until a sufficient depth was reached and was finished by rinsing in distilled water. He was able to achieve hundreds of prints[19]. Berres further reproduced original etched photographs by a process in which an auxiliary intermediate film of Au was electroplated from $AuCl_3$, and numerous Cu replica could be generated by electrotyping. Thus, innumerable photographic reproductions were possible for the first time.

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### Deterioration

Deterioration processes generally observed with common daguerreotypes which contain Hg are absent in the present case. The plate does not contain Hg due to a different fixation process. Moreover, due to the absence of cover glasses – as were used with daguerreotypes – no influence of glass corrosion exists. Since the plate was kept completely open and without any protection during the long period of about 180 years, other corrosion processes could be observed in the present study.

The front side of the plate appears yellow-brownish in the middle and blue-greyish at the blurry edges (Fig. 3 left). It is not known whether the plate was smudged during the manufacture and etching process, or at a later stage, due to inadequate storage and handling. Particularly the left edge of the plate and the pavement area were strongly blurred. In addition, scratches, finger smudges and other blurred areas are visible as fine, dark and grey lines and spots. Due to the numerous grey scales and blurred areas, it was very difficult to distinguish between the physical damages and the chemical alterations of the surface. This suggests that complex deterioration mechanisms took place[1,7].

Unevenness's are visible on the back of the plate (Fig. 9). In the recesses there are residues of a dark coating (probably asphalt).

**Figure 9.** Reverse side of the etched daguerreotype (Fig. 3).

Along the right front side (Fig. 3 left), approx. 15 mm from the edge, a dark stripe can be observed, which probably comes from the mechanical fixture.

Examples of mechanical damages, such as scratches and wiped areas, are presented in Fig.10. Such damages are most probably old and may date back to the time of image production. Several deteriorations exist which look like remnants of splashes. A representative example on the hoof front of the horse's left hindquarter (comp. Fig. 4 right) is depicted in Fig. 10. A SEM image of another splatter reveals the etched morphology within that area (Fig. 11). This may allow the conclusion that the splashes may have been created during or shortly after the production process unintendedly by an etching liquid such as $HNO_3$.

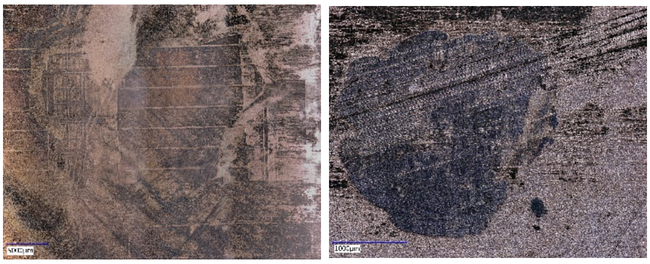

**Figure 10.** Optical micrographs of a spot-like deteriorated area of the etched daguerreotype (Fig. 3).

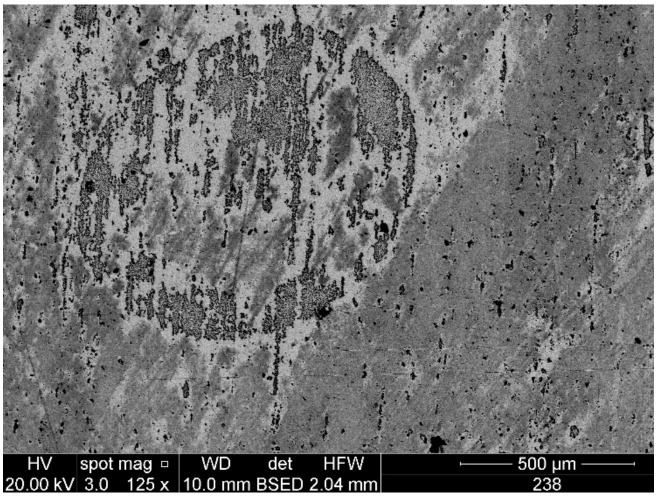


**Figure 11.** Scanning secondary electron micrograph of a spot-like deteriorated area of the etched daguerreotype (Fig. 3).

## Summary

The physico-chemical fundamentals of the world-wide first photographic technology which allowed manifold reproduction has been evaluated (Table 3). This was performed by detailed investigations of a silver-plated copper plate daguerreotype, recently discovered in the collection of the Technisches Museum Wien. It depicts emperor Joseph II's equestrian monument on Josefsplatz in Vienna created most probably by the Viennese photographic pioneers, the brothers Natterer and Joseph Berres. Thus, the chemical processes involved could be identified.

The historically first sensitization process based on the Daguerre's experience was iodization. It resulted in a photosensitive film of AgI. The remarkable invention by the Viennese pioneers, F. Kratochwila, the brothers Natterer, and E. Waidele, consisted in the multiple sensitization of the photographic plates also with chlorine and bromine. On the investigated plate, however, only chlorine was detected. This suggests that in this case solely a chlorine gas treatment was applied so that Ag was oxidized to AgCl.

The common development procedure for daguerreotypes was the formation of Ag amalgam particles next to the latent image Ag clusters. Edmont Becquerel reported a development procedure based on AgI without the use of mercury in 1840, where AgI was converted to latent images (by the "Becquerel effect"). The development technique of the Viennese Natterer brothers in 1841

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could be reconstructed as the hydrolysis of $S_2Cl_2$ resulting in $SO_2$ and $H_2SO_3$, which acted as a reductant for the Ag halides, leading to AgNPs around the latent image Ag nuclei. The Natterer brothers also used $S_2Br_2$ instead of $S_2Cl_2$ and claimed a superb sensitivity. Josef Natterer performed the fixation of the developed image either by potassium cyanide, KCN, or by sodium thiosulphate, $Na_2S_2O_3$ that dissolved the remnant halides. This is supported by the finding that the surface analysis of the investigated plate revealed no Hg.

**Table 3.** Photographic procedure reconstruction.

| Process | Reaction |
|---|---|
| Ag coating of the Cu plate | $2\ [AgCl_2]^- + Cu \rightarrow Cu^{2+} + 4\ Cl^- + 2\ Ag$ |
| Sensitization | $2\ Ag + X_2 \rightarrow 2\ AgX$ |
| Exposure | $8\ AgX + 4\ h\nu \rightarrow 2\ Ag_4 + 4\ X_2$ |
| Development | $2\ AgX + H_2SO_3 + H_2O \rightarrow 2\ Ag + 2\ HX + H_2SO_4$ |
| Fixation | $2\ Na_2S_2O_3 + AgX \rightarrow Na_3[Ag(S_2O_3)_2] + NaX$<br>$4\ KCN + 2\ AgX \rightarrow 2\ K[Ag(CN)_2] + 2\ KX$ |
| Etching | $3\ Ag + NO_3^- + 6\ H^+ \rightarrow 3\ Ag^+ + 3\ H_2O + NO$ |

In the light-exposed area of the plate, a photon-catalysed reduction led to colloidal silver nanoparticles (AgNPs) with a size distribution between 30 nm and 120 nm. This is definitely less than Ag amalgam particle sizes typical for highlight image microstructures of daguerreotypes, which are between 100 nm and 2.5 µm. The colloidal particles exhibited a conversion shell layer consisting of $Ag_2O$, $Ag_2S$, and some AgCl.

The etched plate surface corresponds to low light exposure. In contrast, the high exposure area does not exhibit etching features. The AgNPs and their conversion shells are practically absent in the midtone and dark tone areas. These, in contrast, are dominated by larger etching bits with diameters of 200 – 400 nm. Any conversion layers involving Cl or S are absent while $Ag_2O$ layers are abundant.

Joseph Berres succeeded in developing an etching technique in 1840 for the common daguerreotypes involving Ag amalgams. Thus enabled first reproductions of daguerreotypes. Original literature suggests that the exposed amalgam areas showed a high resistance towards etching with nitric acid. The unreacted AgX could be attacked by the acid. Berres applied a gum arabic solution on the fixed image surface before the etching step.

In the case of the investigated plate without Hg, one can assume that gum arabic was also applied. This treatment resulted in strong wetting of the exposed AgNP regions. The unexposed bulk Ag regions, on the other hand, showed negligible wetting so that preferential etching could take place there. The formed depressions allowed printing ink uptake in the follow-up reproduction step. Berres further reproduced original etched photographs by a process in which an auxiliary intermediate film of Au was electroplated from $AuCl_3$. Thus, innumerable photographic copper replica could be generated by electrotyping for the first time.

Deterioration processes generally observed with common daguerreotypes which contain Hg are absent in the present case. Scratches, finger smudges and blurred areas visible as fine, dark and grey lines and spots are most probably old damages and may date back to the time of image production. Remnants of splashes may have been caused unintendedly during the etching process.

## Conclusion

In 1841, the Viennese Natterer brothers, medical students working together with their colleague Erwin Waidele developed breakthrough photographic procedures providing a hitherto unachieved high sensitivity. These and the first calculated objectives designed by the mathematician Josef Petzval enabled the earliest known photographs of moving street scenes. Joseph Berres was the first to succeed in etching heliogravures for intaglio printing and thus allowed reproducible photographic illustration.

Detailed physico-chemical investigations of the unique silver-plated copper plate daguerreotype depicting emperor Joseph II's equestrian monument on Josefsplatz in Vienna - recently discovered in the collection of the Technisches Museum Wien together with original reports of the involved pioneers – led to the elucidation of the world-first high-sensitivity photographic and reproduction processes.

These findings may serve for the future technological elucidation of early photographs from the first half of the 19th century. Moreover, this will support the recognition and verification of prints manufactured by etched daguerreotypes.

## Experimental Section

A systematic materials analysis of the daguerreotype plate showing the Joseph II's equestrian monument on Josefsplatz in Vienna (Fig. 3 left) has been undertaken. An average Ag-layer thickness was evaluated by x-ray fluorescence (XRF; Roentgenanalytik Systeme GmbH & Co. KG, maXXi 5/PIN). Optical micrographs of the surface topography were recorded with a digital microscope (Keyence, VHX-5000) together with the z-scan techniques. Scanning electron microscopy (SEM) was combined with energy-dispersive X-ray spectroscopy (EDX; QUANTA FEG 250, FEI). The topography was imaged with secondary electron signals. Since secondary electrons are emitted from very close to the specimen surface very high-resolution images could be achieved. The composition was analysed with energy-dispersive X-ray spectroscopy (EDX).

## Competing interests

The authors declare that they have no competing interests.

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